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Research Article

Mechanical and Thermal Properties of Polyamide 1010 Composites Filled with Nanodiamond/Graphitized Carbon Black Nanoparticles

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Abstract

A series of polyamide 1010 (PA1010) composites were prepared by melt technique. A combination of two ball milled nanfillers were used to reinforce the composites i.e. nanodiamond (ND) and graphitized carbon black (GCB). The structure of nanocomposites was characterized by Fourier transform infrared spectroscopy (FTIR). The mechanical tests showed that the tensile strength and Young modulus increased as the ND/GCB content was increased. Compared with pure PA1010, the Young's modulus and tensile strength of PA1010/ND/GCB 20 were significantly improved by 52 % and 22 %, respectively. On the other hand, the elongation at break of PA1010/ND/GCB composites was decreased with the increasing proportion of nanobifiller. For the composites containing 20 wt.% ND/GCB, the elongation at break was decreased to 2 % compared with 5 wt.% loaded PA1010 (25 %) prepared under the same experimental conditions. Scanning electron microscopic (SEM) images showed that the nanobifiller was uniformly dispersed on the fractured surfaces of the nanocomposite and exhibited strong interfacial adhesion with the polyamide matrix. Thermal stability of PA1010/ND/GCB 20 was improved significantly (T_{max} = 530 ℃) relative to 5 wt. % PA1010 composite (T_{max} = 489 ℃) and neat polyamide.

Keywords: PA1010; nanodiamond, graphitized carbon black; ball milling; tensile strength; thermal stability
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1. Introduction

Polymer nanocomposite technology is a rising field in which nanoscale fillers are blended with polymers to fabricate materials with novel characteristics. A wide range of polymers including thermoplastics, thermosets and elastomers have been used to generate nanocomposites. The most commonly used fillers are carbon-based nanoparticles (carbon black, carbon nanotube, graphite), nanoclays, nanosilicas, and nanoceramics. Polymer nanocomposite have the potential to produce materials with considerably enhanced characteristics such as physical, mechanical, electrical, thermal, and barrier properties at low filler contents [1, 2]. Polymer nanocomposite is, therefore, essential alternative to conventional polymer composites. The important factors influencing materials properties are the processing technique, processing parameters, properties of the polymer matrix and type of filler used [3, 4]. Melt mixing has been widely used for the preparation of carbon black-based composites. This method involves mixing of polymer and nano-scale particles with simultaneous heating the mixture above the softening point of the polymer. The mixing process that induces shear force is known as compounding. It is used to disperse the filler in the polymer melt. Internal mixers, two roll mills, extruders, and chaotic mixers are the commonly used types of compounding gears [5, 6]. The composite properties are usually affected by processing technique, process parameters during compounding, selection of the compounding equipment, and morphology of the polymer used [7, 8]. The structure and thermal properties of polyamide 6, polyamide 11 and polyamide 12 have been extensively investigated [9]. Physical properties of polyamide 1010 with longer aliphatic segments have also been studied [10]. The results showed high melting temperature and heat of fusion around 208 ℃ and 132.0 J g^{-1} respectively for the sample annealed at 1.5 GPa. Polyamide and carbon black composites form an important class of polymer composites. Carbon black (CB) is important nanofiller for polymer matrices. CB particles have been melt-blended with polymer matrices to obtain high performance polymer composites [11-13]. Moreover, nanodiamond holds great potential for the mechanical reinforcement of polymer matrices due to its superior hardness and Young's modulus in combination with its huge surface area [14, 15]. The physico-mechanical properties of carbon black loaded polyamide 6 composites have also been investigated [16]. Polyamide 6/modified carbon black (PA6/MCB) composites were prepared in the presence of dispersed carboxyl group modified carbon black (MCB) [17]. The primary aim of this work is to prepare PA1010 nanocomposites by the melt compounding followed by investigation of their mechanical and thermal properties. PA1010 is as an important engineering plastic due to high intensity, elasticity, toughness, and abrasive resistance. The nanofiller opted was the combination of nanodiamond (ND) and graphitized carbon black (GCB). To the best of our knowledge, the PA1010/ND/GCB composite systems have not been reported previously.

2. Experimental

2.1. Materials

Diamond nanopowder (<10 nm particle size, ≥97%) and graphitized carbon black (GCB) (<200 nm) were supplied by Sigma. Commercial PA1010 (viscosity number: O116, relative density: 1.04) was purchased from Shanghai Celluloid Factory (China).

2.2. Instrumentation

IR spectra of the monomers and polymers were taken at room temperature with a resolution of 4 cm^{-1} using Excalibur Series FTIR Spectrometer, Model No. FTSW 300 MX manufactured by BIO-RAD. The SEM images were obtained by Scanning Electron Microscope S-4700 (Japan Hitachi Co. Ltd.). The thermal stability was determined by METTLER TOLEDO TGA/SDTA 851 thermogravimetric analyzer using 5 mg of sample at a heating rate of 10 °C/min under nitrogen atmosphere. The tensile testing was carried out using WP 310 universal material tester. For tensile test, the moulds were made according to ASTM D638 with dimensions of width = 5 mm, thickness = 3 mm and length = 20 mm).

2.3. Ball milling of graphitized carbon black (GCB)

Impurities were removed from the balls through washing with a mixture of $NaCl/H_2O$ and acetone. Ball to powder ratio was kept as 16:1. The 10 g of GCB with 15 large balls and 21 small balls were added into the mill. After 24 h of ball milling, crushed powder was extracted [18].

2.4. Preparation of ND/GCB

Prior to ball milling, impurities from the balls were removed with a mixture of $NaCl/H_2O$ and acetone. The 10 g of nanodiamond and carbon black (1:1 wt. ratio) were placed in ball milling machine. Here again the 15 large balls and 21 small balls were added into the mill and process was started for 24 h. After the required time of milling, the crushed powder was extracted [19].

2.5. Preparation of PA1010/ND/GCB composites by melt mixing

PA1010 composites with various ND/GCB loading (5-20 wt.%) were prepared *via* melt-mixing method. Hacker twin-screw mixer was used at 200 ℃ for 0.5 h (200 rpm) [20].

3. Results and discussion

3.1. FTIR analysis

Fig. 1 shows the structural characterization of and PA1010/ND/GCB 5 and PA1010/ND/GCB 20 using FTIR. Information about the secondary interaction in PA1010/ND/GCB 20 can be acquired by examining the N–H stretching vibration at 3300 cm^{-1} (Fig. 1B). It was found that the band at 3340 cm^{-1} was assigned to ν(NH) for PA1010/ND/GCB 5 (Fig. 1A). This means that increasing amount of nanobifiller developed more interaction with the polyamide so shifting the N–H stretching vibration to lower wave number (40 cm^{-1} lower). The result also indicated that N–C bond length was shortened and there was a closer packing of the polymer chains and filler. The location of the bands at 2921 and 2852 cm^{-1} were assigned to the asymmetric and symmetric stretching vibrations of the CH_2 groups in PA1010/ND/GCB 20. These peaks were also present in the spectrum of PA1010/ND/GCB 5. The $–CH_2–$ vibrations were present at 1189 cm^{-1} (PA1010/ND/GCB 5) and 1175 cm^{-1} (PA1010/ND/GCB 20). Moreover, the characteristic peaks for polyamide carbonyl stretching and N–H bending were present in both the spectra.

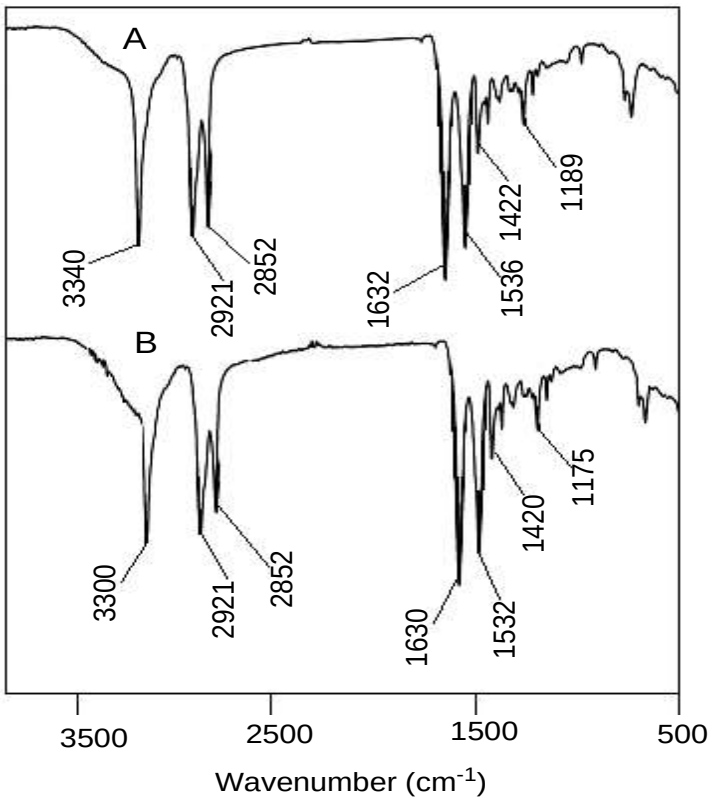

Fig. 1 FTIR spectra of (A) PA1010/ND/GCB 5; and (B) PA1010/ND/GCB 20.

3.2. Mechanical study

In this effort four composite samples with various nanobifiller addition (5-20 wt.%) were prepared by melt route. The corresponding tensile strength, Young's modulus, and elongation at break are summarized in Table 1. Fig. 2 shows the tensile strength of PA1010/ND/GCB nanocomposites. According to the obtained data, the tensile strength of the composites gradually increased with the filler addition. The tensile strength of PA1010/ND/GCB 5 nanocomposite was found as 55 MPa. The tensile strength was increased to 73 MPa with 20 wt. % filler addition. Young's modulus also showed gradual increase with filler addition. Fig. 3 shows the tensile modulus of PA1010/ND/GCB nanocomposite. Increasing the ND/GCB content from 5 to 20 wt.% increased the corresponding Young's modulus from 2.5 GPa to 5.1 GPa. The Young's modulus of PA1010/ND/GCB 20 was 52 % higher than neat matrix. This indicated that the melt technique significantly enhanced the mechanical strength of composites. However, the elongation at break was gradually decreased due to stiffness of the structure. The mechanical properties were also found better than previously reported polyamide composites [21, 22].

Table 1. Mechanical properties of PA1010/ND/GCB nanocomposite.

Sample	Tensile Strength (MPa) ± 0.01	Elongation at break ± 0.01 (%)	Tensile Modulus (GPa) ± 0.01
PA1010	38	35	1.1
PA1010/ND/GCB 5	55	25	2.5
PA1010/ND/GCB 10	62	15	4.3
PA1010/ND/GCB 15	69	10	4.7
PA1010/ND/GCB 20	73	2.0	5.1

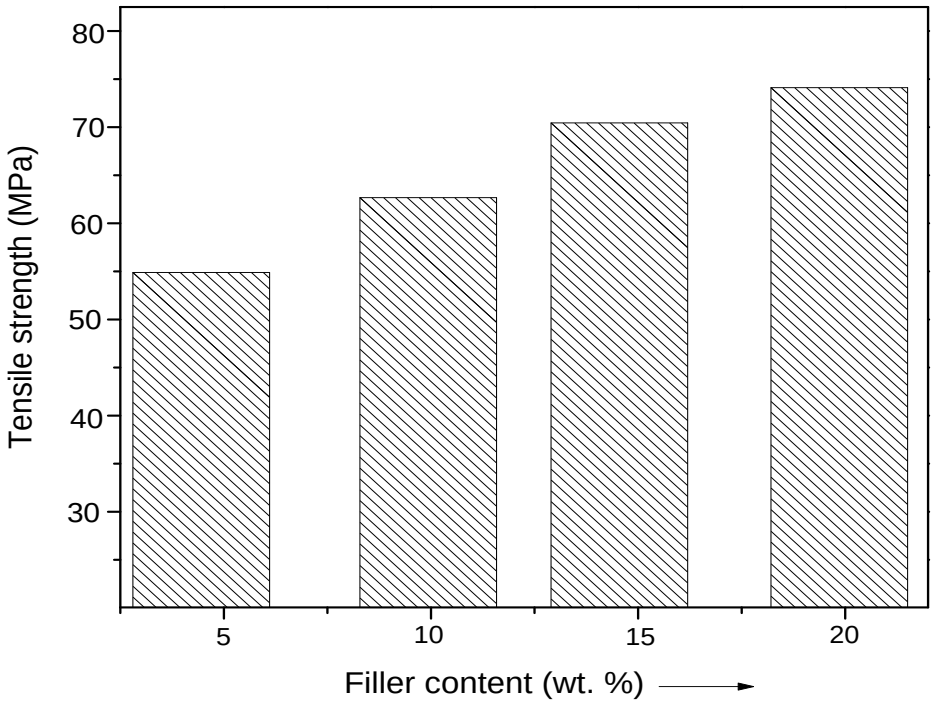

Fig. 2 Tensile strength of PA1010/ND/GCB nanocomposite.

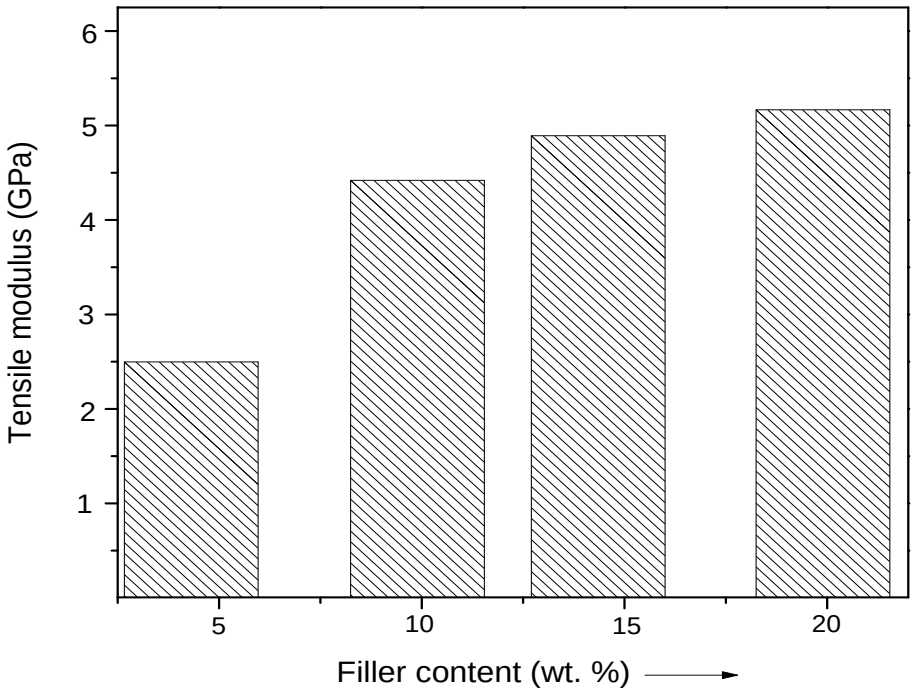

Fig. 3 Tensile modulus of PA1010/ND/GCB nanocomposite.

3.3. Morphology study

Fig. 4 depicts the morphology of the fracture surfaces of the nanocomposites (PA1010/ND/GCB 5, PA1010/ND/GCB 10 and PA1010/ND/GCB 20). It can be seen from the micrographs that the fracture surface of PA1010/ND/GCB 10 (Fig. 4B) presents a much more ordered and denser texture than that of PA1010/ND/GCB 5 (Fig. 4A). Morphological characteristics of a dense and oriented structure were also detected for PA1010/ND/GCB 20 (Fig. 4C). It is apparent that nanobifiller was dispersed uniformly in both these composites (PA1010/ND/GCB 10 and PA1010/ND/GCB 20) and there was no obvious aggregation of ND and GCB bundles in the samples. During the melt compounding process, actually PA1010 coated these nanofillers to prevent any aggregation and formed an even covering layer on ND/GCB. The results suggested that there existed interfacial interaction between the PA1010 matrix and the nanofillers.

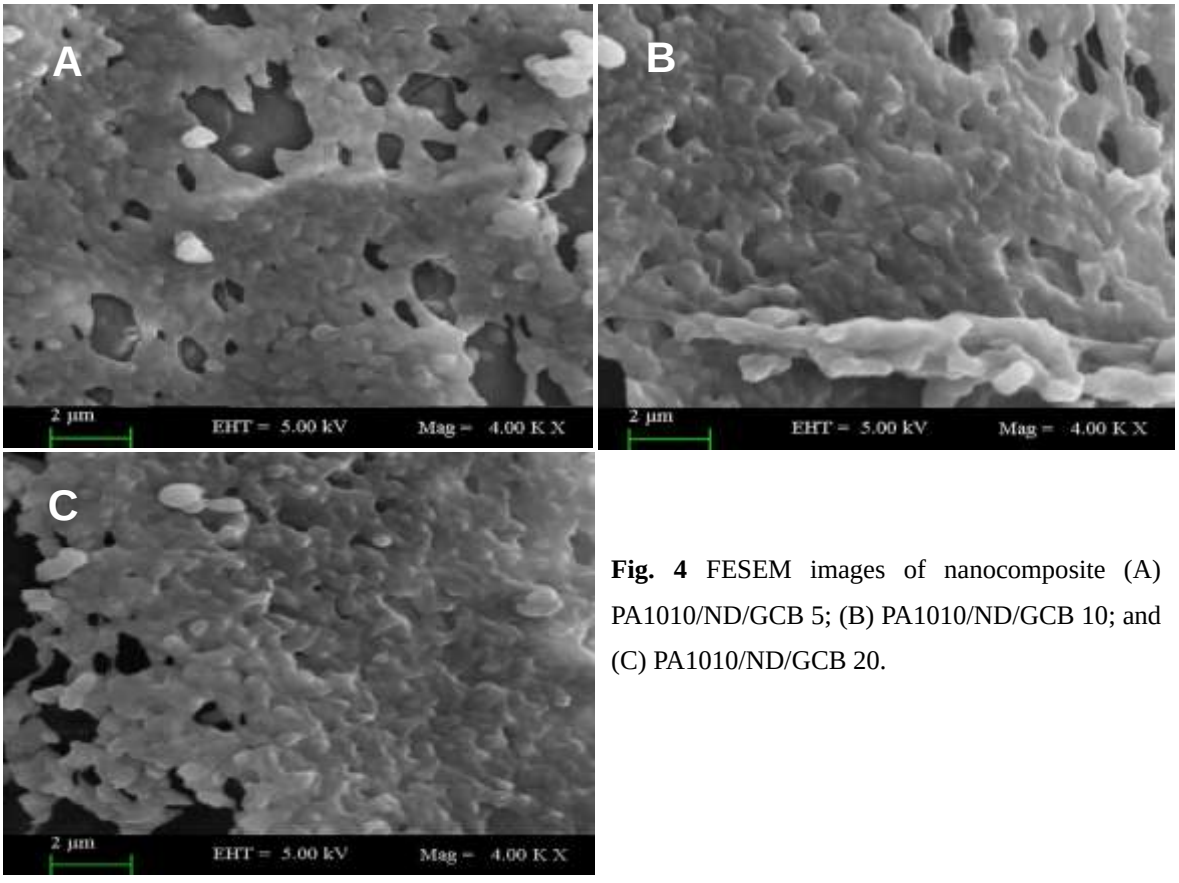

Fig. 4 FESEM images of nanocomposite (A) PA1010/ND/GCB 5; (B) PA1010/ND/GCB 10; and (C) PA1010/ND/GCB 20.

3.4. Thermal analysis

Thermogravimetric analysis was used to study the thermal stability of the composites. Fig. 5 shows TGA curves for PA1010/ND/GCB nanocomposites with loadings of 5, 10, 15 and 20 wt. % nanofiller. The onset temperature (T_0) for thermal degradation increased proportionally with the incorporation of ND/GCB (Table 2). The T_{max} (maximum decomposition temperature) of PA1010/ND/GCB 20 (530 ℃) was significantly higher than the PA1010/ND/GCB 5 (489 ℃) and neat polyamide. The char yield of the materials was also found to increase with filler loading from 10 % (PA1010/ND/GCB 5) to 20 % (PA1010/ND/GCB 10). The results showed that the PA1010 macromolecular chains were deeply interconnected filler. Seeing as the thermal degradation of polyamide started with chain cleavage and radical formation. The nanobifiller ND/GCB worked as radical forager, so delaying the onset of thermal degradation. Thus, the thermal stability of PA1010 matrix was improved. The thermal stability was also found superior to several literature polyamide/CB composites [23-25].

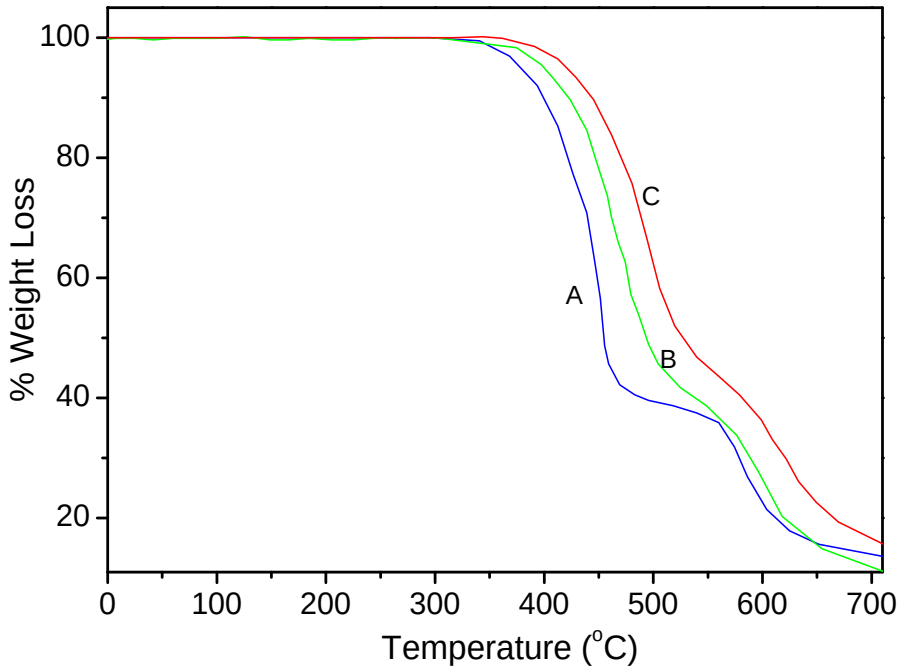

Fig. 5 TGA curves of nanocomposites (A) PA1010/ND/GCB 5; (B) PA1010/ND/GCB 10; and (C) PA1010/ND/GCB 20 at 10 °C/min (N_2).

Table 2. Thermal analyses data of PA1010/ND/GCB nanocomposite.

Sample	T_0 (℃)	T_{max} (℃)	Y_c at 600 ℃ (%)
PA1010	425	460	3
PA1010/ND/GCB 5	435	489	10
PA1010/ND/GCB 10	454	502	15
PA1010/ND/GCB 15	493	509	17
PA1010/ND/GCB 20	510	530	20

T_0: Onset decomposition temperature; T_{max}: Maximum decomposition temperature; Y_c: Char yield; weight of polymer remained

4. Conclusions

The ND/GCB-reinforced PA1010 composites were effectively prepared by melt method and exhibited fine mechanical properties. Mechanical tests on the nanocomposites showed that the tensile strength and Young's modulus were enhanced with the filler addition. The elongation at break, a sign of material toughness, was decreased when ND/GCB was incorporated into the PA1010 matrix. The thermogravimetric analysis showed that the onset thermal degradation temperature and maximum decomposition temperature were considerably increased with the nanobifiller addition. The char yield of the nanocomposites was also increased signifying improved thermal stability. SEM indicated uniform dispersion of ND/GCB throughout the PA1010 matrix. Overall results suggested strong interfacial adhesion between the nanobifiller and the polyamide.

References

1. Bryning M B, Islam M F, Kikkawa J M, Yodh A G. Very low conductivity threshold in bulk isotropic single-walled carbon nanotube-epoxy composites. ***Adv Mater.*** 2005, 17:1186-1191.
2. Kausar A. A Study on Poly(vinyl alcohol-co-ethylene)-graft-Polystyrene Reinforced with two Functional Nanocarbons. ***Polym Plast Technol Engineer.*** 2015, 54:741-749.
3. Kausar A, Wajid-Ullah, Muhammad B and Siddiq M. Influence of Processing Technique on Physical Properties of Modified Polystyrene/Exfoliated Graphite Nanocomposites. ***Mater Manufactur Process.*** 2015, 30:346-355.

4. Zhang W, Dehghani-Sanij A A, Blackburn R S. Carbon based conductive polymer composites. ***J Mater Sci.*** 2007, 42:3408-3418.
5. Athreya S R, Kalaitzidoua K, Das S. Processing and characterization of a carbon black-filled electrically conductive Nylon-12 nanocomposite produced by selective laser sintering. ***Mater Sci Engineer A.*** 2010, 527:2637-2642.
6. Jana S C, Jimenez G A. Electrically conductive polymer nanocomposites of polymethylmethacrylate and carbon nanofibers prepared by chaotic mixing. ***Compos A Appl Sci Manufactur.*** 2007, 38:983-993.
7. Flores A, Cagiao M E, Ezquerra T A, Calleja F J B. Influence of filler structure on microhardness of carbon black–polymer composites. ***J Appl Polym Sci.*** 2001, 79:90-95.
8. Khalil H P S A, Firoozian P, Bakare I O, Akil H Md, Noor A Md. Exploring biomass based carbon black as filler in epoxy composites: Flexural and thermal properties. ***Mater Des.*** 2010, 31; 3419-3425.
9. Yang J, Liu S, Guo X, Luan Y, Su W, Liu J. Annealing of Nylon-1010 under High Pressure. ***Macromol Chem Phys.*** 2002, 203:1081-1087.
10. Yang J, Dong W, Luan Y, Liu J, Liu S, Guo X, Zhao X, Su W. Crystallization and crosslinking of polyamide-1010 under elevated pressure. ***J Appl Polym Sci.*** 2002, 83:2522-2527.
11. Chodak I, Omastova M, Pionteck J. Relation between electrical and mechanical properties of conducting polymer composites. ***J Appl Polym Sci.*** 2001, 82:1903-1906.
12. Foulger, S. H. Reduced percolation thresholds of immiscible conductive blends. ***J Polym Sci Part B: Polym Phys.*** 1999, 37:1899-1910.
13. Meincke O, Kaempfer D, Weickmann H, Friedrich C, Vathauer M, Warth H. Mechanical properties and electrical conductivity of carbon-nanotube filled polyamide-6 and its blends with acrylonitrile/butadiene/styrene. ***Polymer.*** 2004, 45:739-748.
14. Kausar A. Nanodiamond/MWCNT-based Polymeric Nanofiber Reinforced Poly(Bisphenol A-co-epichlorohydrin). ***Malaysian Polym J.*** 2015, 10:23-32.
15. Ullah M, Kausar A, Siddiq M, Subhan M, Zia M A. Reinforcing Effects of Modified Nanodiamonds on the Physical Properties of Polymer-based Nanocomposites: A Review. ***Polym Plast Technol Engineer.*** 2015, 54:861-879.
16. Basavaraja E, Ramaraj B, Lee J -H, Siddaramaiah. Polyamide 6/carbon black/molybdenum disulphide composites: Friction, wear and morphological characteristics. ***Mater Chem Phys.*** 2013, 138:658-665.
17. Liu Y, Xu W, Zhu J, Wang C, Sheng S. Polyamide 6/modified Carbon Black Nanocomposites Prepared via In Situ Polymerization. ***J Macromol Sci B Phys.*** 2015, 54:469-480.
18. Yadav T P, Yadav R M, Singh D P. Mechanical Milling: a Top Down Approach for the Synthesis of Nanomaterials and Nanocomposites. ***Nanosci Nanotechnol.*** 2012, 2:22-48.
19. Spitalskya Z, Tasis D, Papagelis K, Galiotis C. Carbon nanotube–polymer composites: Chemistry, processing, mechanical and electrical properties. ***Prog Polym Sci.*** 2010, 35:357-401.
20. Kausar A, Hussain S T. Synthesis and properties of melt processed poly(thiourea-azo-sulfone)/carbon nanotubes nanocomposites. ***Chinese J Polym Sci.*** 2014, 32:64-72.

21. Zhou K, Gu S -Y, Zhang Y -H, Ren J. Effect of dispersion on rheological and mechanical properties of polypropylene/carbon nanotubes nanocomposites. ***Polym Engineer Sci.*** 2012, 52:1485-1494.
22. Athreya S R, Kalaitzidoua K, Das S. Processing and characterization of a carbon black-filled electrically conductive Nylon-12 nanocomposite produced by selective laser sintering ***Mater Sci Engineer. A*** 2010, 527:2637-2642.
23. Socher R, Krause B, Hermasch S, Wursche R, Pötschke, Electrical and thermal properties of polyamide 12 composites with hybrid fillers systems of multiwalled carbon nanotubes and carbon black. ***Compos Sci Technol.*** 2011, 71: 1053-1059.
24. Petrovicova E, Knight R, Schadler L S, Twardowski T E. Nylon 11/silica nanocomposite coatings applied by the HVOF process. II. Mechanical and barrier properties. ***J Appl Polym Sci.*** 2000, 78:2272-2289.
25. Arroyo M, López-Manchado M A, Herrero B. Organo-montmorillonite as substitute of carbon black in natural rubber compounds. ***Polymer.*** 2003, 44:2447-2453.